

Phonons of Metallic Vicinal Surfaces

Abdelkader Kara* and Talat S. Rahman

*Department of Physics, Cardwell Hall, Kansas State University, Manhattan,
Kansas 66506, USA*

**Corresponding author: e-mail: akara@ksu.edu, FAX: 785 532 6806*

Abstract

We present an analysis of the vibrational dynamics of metal vicinal surfaces using the embedded atom method to describe the interaction potential and both a real space Green's function method and a slab method to calculate the phonons. We report two main general characteristics : a global shift of the surface vibrational density of states resulting from a softening of the force field. The latter is a direct result of the reduction of coordination for the different type of surface atoms; and an appearance of high frequency modes above the bulk band, resulting from a stiffening of the force field near the step atom. The latter is due to a rearrangement of the atomic positions during the relaxation of the surface atoms yielding a large shortening of the nearest neighbor distances near the step atoms.

Keywords: surface relaxation; surface structure, morphology; copper; nickel;
vicinal single crystal surfaces; surface waves, phonons

1 Introduction

Steps at crystal surfaces have been known to play an important role in several phenomena including epitaxial growth and heterogeneous catalysis. The soaring of the technological advances occurring during the last few decades is due to a better understanding of the behavior of materials. The properties of certain materials become richer as their structures become more complex. The simplest aspect of complexity in materials structure is the loss of neighbors resulting in a reduction of coordination. A simple picture would imply that the lower the coordination, the larger the rearrangement of electronic and ionic structures. In the case of stepped surfaces in particular, it was pointed out by Smoluchowsky [1] that an electronic relaxation at the step could lead to a de-population of surface states at that locality, a view supported later by several calculations [2] -[4]. The lower coordination and the reduced symmetry of atoms on vicinal surfaces, as compared to those in the bulk solid and on flat surfaces, lead to characteristic variations in the surface electronic charge densities which may in turn affect the reactivity and the propensity to harbor localized vibrational and electronic surface excitations. Early interest in vicinals was motivated by the need to comprehend in a rather controlled manner the sensitivity of catalytic reactions [5] to atoms in step and kink sites. Attention on vicinal surfaces has renewed in recent years, because of their technological importance as templates [6] for the growth of well ordered, laterally patterned nanostructures. For such technological purposes there is also the need to understand the stability of vicinal surfaces as a function of surface temperature. The presence of the surface, the step, and the kink can be thought of as perturbations of increasing complexity on an otherwise periodic system. On flat surfaces the reduction in translational symmetry in the direction perpendicular to the surface leads to localized surface vibrational modes whose frequencies, though distinct from the bulk modes, lie within the bulk phonon band. The frequencies of surface localized modes at Brillouin zone

boundaries have been of particular interest as the extent to which they lie below the bulk band serves as a measure of the changes in surface force constants from values in the bulk [7]. Recent experiments using He atom-surface scattering technique have also unveiled such low frequency, step localized mode on vicinals of Cu [8] and Ni [9]. On the other hand, in early efforts to measure phonons at metal surfaces Ibach and Bruchmann [10] had found a mode on Pt(775), using electron energy loss spectroscopy (EELS), whose frequency was higher than bulk phonon band. It is the purpose of this paper to demonstrate that these two opposite behaviors (a shift towards low frequencies and a stretch beyond the top of the bulk band) of the vibrational dynamics are general characteristics of vicinal surfaces.

The paper is divided in three sections. In the next section, we present details about the geometry of vicinal surfaces and theoretical details. In section III, we present the vibrational dynamics of Ni(977) as an illustration of the softening of the force field near the step. Phonons of Cu vicinal surfaces will be used in section IV to illustrate the stiffening of the force field near the step and finally, in section V we present concluding remarks.

2 Theoretical Details

Vicinals are surfaces for which the macroscopic orientation forms a small angle with respect to a low index plane. Ideally, they are made up of terraces separated by regularly spaced steps of mono-atomic height. The Ni(977) surface is a vicinal of Ni(111) fabricated by cutting Ni(111) at an angle of 7° from the (111) plane. It consists of (111) terraces containing eight $\langle 01\bar{1} \rangle$ chains, and a (100) step face. As shown in Fig. 1, the x and y axes are in the (977) plane and are, respectively, perpendicular to and along the step, while the z axis is perpendicular to the (977) plane. A side view of (977) appears in Fig 1, and

the centered rectangular surface Brillouin zone, along with the top view, is also shown in Fig. 1.

For the interaction potential between atoms in the Ni and Cu vicinals, we use the many-body, embedded atom method (EAM) [11,12] potential. This interatomic potential has proved to be quite successful in describing a variety of properties in the bulk and at the surfaces and interfaces for six fcc metals: Cu, Ag, Ni, Pd, Pt and Au. We have also obtained reliable results for the dynamics of Cu, Ag and Ni surfaces [13], and for the energetics of Cu vicinals [14] within the EAM potentials. For Ni(977), as in the case of Cu vicinals, after constructing the system in the bulk truncated positions, we apply standard conjugate gradient, as well as, annealing-quenching procedures to determine the minimum energy configuration. The two methods yield the same minimum energy configuration, which is found to display complex relaxation patterns.

To calculate the vibrational density of states we use two methods: a real space Green's function method (RSGF) and a slab method, in the harmonic approximation. The advantage of a RSGF method is that one calculates the total density of states with no a-priori choice of wave-vector, as would be the case in calculations based on 'k-space'. Also one can get the polarization of the vibrational modes from the imaginary part of the columns of the Green's functions associated with the system at hand. This method exploits the fact that for a system with a finite range of interatomic interactions, the force constant matrix can always be written in a block tridiagonal form [15] in which the sub-matrices along the diagonal represent interactions between atoms within a chosen local region and the sub-matrices along the 'off-diagonal' correspond to interactions between neighboring localities. Thus an infinite/semi-infinite system is converted quite naturally into an infinite/semi-infinite set of local regions. The real space Green's function method also has an advantage over the familiar 'continued fraction' method [16] as it does not involve truncation schemes to determine the recursion coefficients, rather a more general

and simpler recursive scheme is applied [17], which has been successfully used for the study of the phonons of Au vicinals [18]. The vibrational density of states $N_l(w)$ corresponding to locality "l" is related to the trace of the Green's function by the well known relation

$$\rho_l(\omega^2) = -\frac{1}{3n_l\pi} \lim_{\epsilon \rightarrow 0} \left\{ \text{Im}[\text{Tr}(G_{ll}(\omega^2 + i\epsilon))] \right\} \quad (1)$$

with $N_l(w) = 2w\rho_l(\omega^2)$, where G_{ll} is the Green's function sub-matrix associated with locality "l" and n_l is the number of atoms in this locality.

For the slab method [19] we proceed as follows. With the atoms in the equilibrium configuration, the force constant matrix needed to calculate the vibrational dynamics of the system is extracted from the partial second derivatives of the EAM potentials. The secular equation with the dynamical matrix is then diagonalized in a straight forward manner to obtain the phonon frequencies and displacement patterns from the eigenvalues and eigenvectors of the diagonalized matrix.

3 Vibrational Dynamics of Ni(977) : softening of the force field

The calculated local density of states (LDOS) for the step and the terrace atoms of Ni(977) are compared with those for the Ni(111) surface atoms in Fig. 2. we note that the LDOS of the Ni(977) terrace atoms is almost identical to the one of Ni(111). This result is a good indicator that changes due to the creation of steps is highly localized in nature. The other interesting feature in Fig. 2 is a global shift of the step atom low frequency band to even lower frequencies, as compared to the modes associated with the terrace (and Ni(111) surface atoms). This is a direct signature of an extra softening of relevant force constants, due to a loss of five neighbors, in agreement with suggestions of Niu et al. [9]. To appreciate the implications of the loss of neighbors for

the Ni(977) step atoms, we now turn to an examination of the force constant matrices associated with them. As seen from Table I, the reduction in the coordination results in a large softening of the force constant matrix elements between two step atoms : 71% along x (k_{xx}) and 13.7% along y (k_{yy}), as compared to their counterparts in the bulk. Note that on Ni(111), k_{yy} , between neighboring atoms in the top layer, is reduced by 5.7% from the bulk value.

For flat surfaces, the loss of neighbors in the direction perpendicular to the surface is the cause of the appearance of a surface mode (the so called Raleigh mode) with an atomic displacement perpendicular to the surface and an in plane propagation. This is a quasi 2 dimensional mode as the displacement amplitude decays exponentially into the bulk. Unlike the flat surface, vicinal surfaces present an equivalency between atoms belonging to the same chain and hence, we expect that this 1D equivalency would cause the appearance of a quasi-1D mode. The mode at 3.3 THz is a quasi-one-dimensional (Q1D) with the following characteristics (Fig. 3): it involves only the concerted motion of the step and corner atoms in conjunction with that of the terrace chain of atoms next to the step (transparent atoms in Fig.3). The step atoms alternate with displacement vectors $(+1.0, 0.0, -0.67)$ and $(-1.0, 0.0, +0.67)$, the corner atoms with vectors $(+0.27, 0.0, -1.0)$ and $(-0.27, 0.0, +1.0)$, and the terrace atoms with vectors $(0.0, +0.24, 0.0)$ and $(0.0, -0.24, 0.0)$. Thus the step and the corner atoms move in the xz plane, while the terrace atoms move along the y direction to accommodate the propagation of this mode along the y axis which lies parallel to the step. The rest of the atoms are at rest. The wavelength of this mode is $2 \times \text{nearest neighbor distance}$ or 4.978 \AA and its wave-vector $q = (0.0, 1.262 \text{ \AA}^{-1}, 0.0)$. It is thus a mode at \bar{Y} (this is \bar{K} of the (111) surface Brillouin zone) shown in Fig. 1. This is a *super* localized mode since the motion is restricted to the step atoms and their immediate neighbors on the surface in good agreement with the experimental observation [9].

4 Vibrational Dynamics of Cu vicinals : stiffening of the force field

We showed in the previous section that the step LDOS presents a global shift towards the low frequencies and the question is whether this global shift is also experienced by the high frequency band. About two decades ago, Ibach and Bruchmann [10] found a mode on Pt(775), using electron energy loss spectroscopy (EELS), whose frequency was higher than that of the Pt bulk phonon spectrum. The appearance of this mode was later shown to be due to a stiffening of the force field near the step [20]. Such mode was also found on Au(511) [18] and Ni(977) [21]. Our recent systematic study of the vibrational dynamics and thermodynamics of several vicinals of the (100) and (111) surfaces of Ag, Cu, Ni and Pd [22] of varying terrace width (3 to 10 atoms) provides further evidence that the presence of localized modes above the bulk band is a characteristic of vicinal surfaces of metals obeying the bond-length bond-order correlation. This characteristic can be traced to the stiffening of some force constants of the step atoms. In this section we present only selected results for copper vicinals, of two types. The first set is that of Cu(511), Cu(711), Cu(911) and Cu(17,1,1) which are vicinals of Cu(100) with terraces 3, 4, 5 and 9 atoms wide, respectively. The other set comprises Cu(211) and Cu(331) which are vicinals of Cu(111) with 3 atoms-wide terraces, and, respectively, a (100) and (111)-microfaceted step face [23].

To illustrate the appearance of modes above the bulk phonon band and its correlation to the stiffness of specific force constants, we consider here the case of Cu(211). In Fig. 4, we show the projected vibrational density of states, at the $\bar{\Gamma}$, \bar{X} and \bar{Y} points for the step (SC), BNN (see figure 1), and bulk atoms. For clarity, we present here only the z (perpendicular to surface) component of the Local density of states. In Fig. 4a, at the $\bar{\Gamma}$ point, near the top of the bulk band, we note two modes involving both the SC and BNN atoms, one mode just below the top of the bulk band and another one above it. We note that

for both modes, the amplitude is much larger for the BNN than for SC. In Fig. 4b, at the \bar{X} , these high frequency modes present the lowest amplitude. Instead, we find resonance modes inside the bulk band and localized surface modes beyond the bulk band and in the "stomach" gaps as discussed in detail previously [24]. The largest signature of the high frequency mode, relative to the bulk, occurs at the \bar{Y} point (Fig. 4c) in the surface Brillouin zone. Features similar to those in Fig. 4 have been found for all vicinals of the two sets considered here. The shifts of these high frequency modes above the bulk band for Cu(211), Cu(511) and Cu(17,1,1) are shown in Table II. In the first column, we report the relative change in the bond length between the SC and BNN atoms and in the second column we show the relative change in the z-component of this bond. Note that in all cases the reduction of the bond length is dominated by a reduction of the z component of the bond. The shift of the frequency above the top of the bulk band is higher for Cu(17,1,1) than that for Cu(211) and Cu(511) implying a stronger relaxation of Cu(17,1,1) due to a relief of step-step interaction. The reason for choosing the three surfaces in table II was the availability of experimental data [24]. As has been discussed in detail in Ref[24], EELS data reveal a mode above the bulk band for Cu(211) but not on the other two surfaces. We await further studies to settle this issue.

To link this shift of the frequency above the top of the bulk band to the change of the force field near the step, we show in tables III and IV the force constants associated with the step atom, on the one hand, and the corner, the BNN and the terrace atom, on the other. The most important stiffening occurs for k_{zz} of the force constant matrix between the step atom and the BNN. This is responsible for the large amplitude of the high frequency mode associated with the BNN [24]. The stiffening of k_{zz} between the SC and BNN in the case of (17,1,1) is twice that of Cu(211) and Cu(511) [24] resulting in the larger shift mentioned above, further illustrating the correlation between the stiffening of this k_{zz} to the appearance of high frequency modes. In Ref[24], we

also reported an even higher shift above the bulk band in the case of the kinked surface Cu(532) associated with an even larger stiffening of the appropriate k_{zz} .

This large stiffening of the force field is actually due to a shortening of the nearest neighbor distance between the step atom and its neighbors (except for the neighbor on the same step chain). As the step atoms lose 5 neighbors, the electronic charge density is strongly perturbed and a rearrangement of the electronic structure is accompanied by a strong rearrangement of the ionic positions hence lowering the total energy of the system. We find the shortening of the bond length near the step to be a general feature of the stepped surfaces and independent of the terrace width and the terrace geometry. As an example, we illustrate in Fig. 5 the change in the bond lengths of the step atom with its nearest neighbors for vicinals with 3-atom wide terraces with different geometries: Cu(511) a vicinal of (100) with a (111) step face, Cu(211) a vicinal of (111) with a (100) step face and Cu(331) a vicinal of (111) with a (111) step face. All 3 surfaces show the same general trend of a shortening of the bond length near the step [23]. In the case of Cu(211), there is a general and quantitative agreement between EELS data [25], *ab initio* calculations [26] and EAM calculations [23]. In Fig. 6 we present the same effect for vicinals of (100) with different terrace widths. We note again that the bond length associated with the step atom is always shortened.

5 Conclusions

We have focussed in this paper on two characteristics of the vibrational modes of vicinal surfaces consisting of two distinct results: the softening and the stiffening of the force constants associated with the step atoms.

The vibrational local density of states (LDOS) of the step atoms shows a distinct global shift towards the low frequencies, as compared to that of terrace atoms, and is attributed to softening of some force constants associated with the step atoms. For the case of Ni(977), the result is in qualitative agreement with He scattering data of Niu *et al* [9].

We have also presented here arguments about the existence and origin of modes above the bulk band on several vicinals of Cu. Our lattice dynamical calculations show that the high frequency modes (above the bulk phonon band) are a natural feature of metal vicinal surfaces and should be present at least on those surfaces whose dynamics could be described adequately by potentials like the EAM which assume that the electronic charge distributions to be spherically symmetric and follow bond-length bond-order correlation. The high frequency modes are due to a stiffening of the force field near the step resulting from a global shortening of the nearest-neighbor distances associated with the step atom. Since the BNN atom has already a perfect coordination of 12, a further shortening of the distance between the BNN and the step atom causes the former to present a high frequency mode with the highest amplitude. As mentioned, these conclusions about the high frequency modes have been verified experimentally in the case of Cu(211) [24]. While we are now engaged in performing *ab initio* calculations to further test the reliability of our results, we also await other experimental data to shed more light on the matter.

In summary, a large reduction in the coordination of the step atoms yields a substantial softening of the force constants between step atoms along the same chain which causes a very strong and complex rearrangements of the atomic positions resulting in a shortening of the bond and hence also a stiffening of the force field near the step. These structural and dynamical changes localized in the vicinity of the step has important consequences for the thermodynamic properties of vicinal surfaces [23]. Because of the localized nature of the char-

acteristics presented here, we are now in a position to extend these conclusions to metallic nanoclusters [27].

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Figure Captions

Figure 1: Geometry of Ni(977) : side view (top) and top view with surface Brillouin zone (bottom). SC= Step Chain, TC= Terrace Chain, CC= Corner Chain and BNN= Bulk Nearest Neighbor (of the step atom).

Figure 2: Local density of states for Ni(977) step and terrace atoms, and for a Ni(111) surface atom.

Figure 3 : Polarization of the Q1D mode at 3.3 THz . The arrows pointing out of the spheres describe the amplitude of the displacements. The moving atoms are transparent.

Figure 4 : The z-component of the projected vibrational density of states, at Γ (a), \overline{X} (b) and \overline{Y} (c) points for step (dashed), BNN (dot-dashed) and bulk (solid line) atoms for Cu(211).

Figure 5: Shortening of the bond length between the step atom and it's neighbors for the three vicinals with terraces 3 atoms wide.

Figure 6: Shortening of the bond length between the step atom and it's neighbors for the three vicinals with terraces 4 (Cu(711)), 5 (Cu(911)), and 9 (Cu(17,1,1)) atoms wide.

Table 1

Illustration of the softening of the force field, the force constants are in (eV/ \AA /unit mass): Ni(977).

ATOMS		SURFACE			BULK		
		x	y	z	x	y	z
	x	0.0236	0.1489	0.0044	0.0816	0.0000	0.0058
SC-SC	y	-0.1489	<u>-2.6386</u>	-0.2796	0.0000	<u>-3.0568</u>	0.0000
	z	0.0044	0.2796	-0.0050	0.0058	0.0000	0.0805

Table 2

Calculated percentage changes (Δr) in bond length, its vertical component (Δz), between the step atom and its bulk nearest neighbor (BNN), for three Cu vicinal surfaces. Here ($\Delta\nu$) is the shift in the frequency of the step localized mode above the maximum bulk mode.

Surface	Δr (%)	Δz (%)	$\Delta\nu$ (THz)
Cu(211)	-2.1	-2.7	+ 0.24
Cu(511)	-2.3	-2.9	+ 0.24
Cu(17,1,1)	-2.4	-2.7	+ 0.43

Table 3

Illustration of the stiffening of the force field, the force constants are in (eV/Å/unit mass): Cu(511).

ATOMS		SURFACE			BULK		
		x	y	z	x	y	z
SC-TC	x	<u>-2.1859</u>	0.0000	-0.8307	<u>-1.8234</u>	0.0000	-0.5452
	y	0.0000	0.0678	0.0000	0.0000	0.0875	0.0000
	z	-0.3896	0.0000	-0.1067	-0.5452	0.0000	-0.0499
CC-SC	x	<u>-0.9416</u>	-0.7116	0.6304	<u>-0.8418</u>	-0.7037	0.7594
	y	-0.7637	-0.4282	0.4892	-0.7037	-0.4205	0.5598
	z	0.8832	0.6337	-0.5432	-0.7594	0.5598	-0.5238
BNN-SC	x	-0.0683	0.3926	-0.5996	-0.0769	0.3062	-0.4846
	y	0.3822	-0.5201	1.0726	0.3062	-0.4205	0.8454
	z	0.6337	1.1648	<u>-1.7441</u>	-0.4846	0.8454	<u>-1.2888</u>

Table 4

Illustration of the stiffening of the force field, the force constants are in (eV/Å/unit mass): Cu(211).

ATOMS		SURFACE			BULK		
		x	y	z	x	y	z
SC-TC	x	<u>-1.3793</u>	0.8954	-0.6340	<u>-1.2838</u>	0.8500	-0.4907
	y	0.8727	-0.4276	0.3859	0.8500	-0.4204	0.2932
	z	-0.3259	0.2036	-0.1298	-0.4907	0.2932	-0.0818
CC-SC	x	<u>-1.6344</u>	0.0000	1.0355	<u>-1.2837</u>	0.0000	0.9814
	y	0.0000	0.0898	0.0000	0.0000	0.0875	0.0000
	z	1.3683	0.0000	-0.7534	0.9814	0.0000	-0.5897
BNN-SC	x	0.1237	0.0162	-0.0582	0.0931	-0.0069	-0.0040
	y	-0.0140	-0.5070	1.1120	-0.0069	-0.4204	0.8991
	z	-0.0770	1.9530	<u>-1.9071</u>	-0.0040	0.8991	<u>-1.4587</u>











